

A. "Laboratory Spectroscopy in Support of Atmospheric Measurements"

RTOP # 147-23-02

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C. Abstract of Research Objectives

Optical Measurements of Trace Species in the atmosphere require precise, accurate spectroscopic data for the molecules under study. This laboratory exists to provide high quality spectroscopic data for the interpretation of data from existing satellite balloon, ground and aircraft instruments, as well as to provide sufficient data to assess the feasibility of new instruments.

D. Summary

Work in FY 89 has centered the time resolved, rotationally resolved fluorescence spectroscopy in OH radicals. The importance is derived from fluorescence lidar measurements of OH in the stratosphere, and a need to understand the collisional redistribution of energy in the excited state in order to interpret the field measurements. The laboratory has studied effects of collisions with O₂ and N₂ on excited state OH molecules for both the v'=0 and v'=1 levels. In addition to electronic quenching rates, total

deactivation out of populated rotational levels has also been measured. This work is currently being expanded to include measurements at stratospheric temperatures.

E. Publications

1. "Collisional Deactivation and Rotational Transfer Rates in the $A^2\Sigma^+(v'=1)$ State of OH," J. Burris, J. Butler, T. J. McGee and W. S. Heaps, Chem. Phys., 124, 251, 1988.
2. "Quenching and Rotational Transfer Rates in the $A^2\Sigma^+(v'=0)$ Manifold of OH," J. Burris, J. Butler, T. J. McGee, and W. S. Heaps, to be submitted to Chemical Physics.

A. DETERMINATION OF SPECTROSCOPIC PROPERTIES OF ATMOSPHERIC MOLECULES
FROM HIGH RESOLUTION VACUUM ULTRAVIOLET CROSS SECTION AND WAVELENGTH
MEASUREMENTS

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C. ABSTRACT OF RESEARCH OBJECTIVES

The research objectives are (a) the comprehensive high resolution spectroscopic investigation of the absorption spectra, cross sections and the predissociation line widths of the Schumann-Runge bands of oxygen in the wavelength region 175-205 nm and the determination of improved absorption continuum cross sections of oxygen in the 205-240 nm region of the Herzberg continuum; and (b) the measurement of the absolute absorption cross section of ozone, and its temperature dependence, in the region 180-340 nm. These absorption bands play a critical role in the photochemistry of the upper atmosphere.

D. SUMMARY OF PROGRESS AND RESULTS

Cross sections of $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ at 79 K have been obtained from photoabsorption measurements in the wavelength region 177-198 nm with a 6.65 m photoelectric scanning spectrometer. The measured absorption cross sections of the $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ Schumann-Runge bands (11,0) through (3,0) are independent of the instrumental width. The measured cross sections are presented graphically and are available at wavenumber intervals of $\sim 0.1 \text{ cm}^{-1}$ on magnetic tape from the National Space Science Data Center, NASA/Goddard Space Flight Center. Band oscillator strengths have been determined by numerical integration of the measured absolute cross sections and are in agreement with our theoretically calculated values.

High resolution absorption spectra of $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ have been photographed, at 300 K and 78 K, throughout the region 175-205 nm. Precise wavelength measurements and rotational analyses of the Schumann-Runge bands have been completed. Spectroscopic constants of the $B^3\Sigma_u^-$ states have been determined. The concept of mass-reduced vibrational quantum numbers has been used to combine isotopic molecular constants from $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$. Values of molecular constants have been obtained by interpolation for bands with unresolved triplet structure. Excellent agreement between calculated and experimental level shifts has been obtained for all three isotopic molecules.

The laboratory values of the Herzberg continuum absorption cross section of oxygen at room temperature from Cheung *et al.* [Planet. Space

Sci. (1986) 34, 1007] and Jenouvrier et al. [Planet. Space Sci. (1986) 34, 253 and J. Quant. Spectrosc. Radiat. Transfer (1986) 36, 349] have been compared and reanalyzed. These values have been combined to obtain improved values of the Herzberg continuum cross section throughout the wavelength region 205-240 nm.

We have completed measurements of the absorption cross sections of the Schumann-Runge bands in the window regions between the rotational lines in the wavelength region 180-195 nm. The measurements have been done with many different pressures of oxygen, 50-760 Torr, so that the pressure dependent absorption can be separated from the main cross sections.

Measurements of the absolute absorption cross section of ozone at the temperatures 195 K, 228 K, and 295 K have been made at discrete wavelengths in the region 238-335 nm. Our absolute cross sections have been used to put our recent relative cross section measurements on a firm absolute basis.

E. JOURNAL PUBLICATIONS

Absolute Absorption Cross Section Measurements of Ozone in the Wavelength Region 238-335 nm and the Temperature Dependence, K. Yoshino, D.E. Freeman, J.R. Esmond, and W.H. Parkinson, Planet. Space Sci. 36, 395-398 (1988).

Wavelength Measurements and Analysis of the Schumann-Runge Bands of $^{18}\text{O}_2$ in the Region 175-205 nm, A.S.-C. Cheung, K. Yoshino, D.E. Freeman and W.H. Parkinson, J. Mol. Spectrosc. 131, 96-112 (1988).

High Resolution Absorption Cross Sections and Band Oscillator Strengths of the Schumann-Runge Absorption Bands of Isotopic Oxygen, $^{18}\text{O}_2$, at 79K, K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. 36, 1201-1210 (1988).

Improved Absorption Cross Sections of Oxygen in the Wavelength Region 205-240 nm of the Herzberg Continuum, K. Yoshino, A.S.-C. Cheung, J.R. Esmond, W.H. Parkinson, D.E. Freeman, S.L. Guberman, A. Jenouvrier, B. Coquart, and M.F. Merienne, Planet. Space Sci. 36, 1469-1475 (1988).

The Schumann-Runge Bands of $^{16}\text{O}^{18}\text{O}$ in the Wavelength Region 175-205 nm and Spectroscopic Constants of Isotopic Oxygen Molecules, A.S.-C. Cheung, K. Yoshino, D.E. Freeman R.S. Friedman, A. Dalgarno and W.H. Parkinson, J. Mol. Spectrosc. 134, 362-389 (1989).

High Resolution Absorption Cross Sections and Band Oscillator Strengths of the Schumann-Runge Absorption Bands of Isotopic Oxygen, $^{16}\text{O}^{18}\text{O}$, at 79K, K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. 37, 419-426 (1989).

A. INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF STRATOSPHERIC MEASUREMENTS INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF ATMOS

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C. ABSTRACT OF RESEARCH OBJECTIVES

The objective of this program is the acquisition and analysis of molecular spectral parameters for the 2 to 16 μm region in order that data obtained from stratospheric measurements programs can be properly interpreted. Field instruments such as the Atmos and Mark IV interferometers have spectral resolutions of 0.01 cm^{-1} and 0.005 cm^{-1} , respectively, which require that laboratory measurements, which support these efforts, be obtained at comparable or better spectral resolutions.

For this program, conventional spectroscopic techniques are used to analyze infrared spectra obtained in the laboratory. Spectra are recorded at 0.0028, 0.005 and 0.01 cm^{-1} resolutions using an interferometer located in the McMath facility at the Kitt Peak National Observatory. The gases studied include the normal trace species such as H_2O , CO_2 , CH_4 , and N_2O and less abundant trace gases such as H_2CO , NO_2 , COF_2 , and CH_3Cl . The molecules of the first category produce absorptions over wide expanses of the stratospheric spectrum which, in many cases, overlap or blend with spectral features of the less abundant species. Therefore, in order to obtain an accurate estimate of the stratospheric concentration of the less abundant gases using infrared techniques requires not only an accurate estimate of the line parameters of these species but also a detailed knowledge of the line parameters of the normal trace gases.

D. SUMMARY OF PROGRESS AND RESULTS

Our efforts have been focused on compiling accurate spectral parameters derived from laboratory measurements for use in the reduction of stratospheric data. A large portion of this compilation has already been used in the various analysis of ATMOS spectra obtained from Spacelab 3. Listings of spectral parameters derived from our laboratory measurements which are presently available to ATMOS investigators include the following: N_2O (500-4100 cm^{-1}), CH_4 (1100-4700 cm^{-1}), NO_2 (1520-1660 cm^{-1}), HDO (1000-4400 cm^{-1}), CO_2 (1200-1400 cm^{-1}), and H_2^{16}O , H_2^{17}O , and H_2^{18}O (900-4400 cm^{-1}).

During 1988 and 1989, additional spectra of water vapor (four isotopic species), methane (two isotopic species), methyl chloride and calibration standards were obtained with a Fourier transform spectrometer located at the Kitt Peak National Observatory (KPNO). Also on computer files, we have a large number of spectra of other molecules (N_2O , NO_2 , CO_2 , CO , COF_2 , HNO_3 , HCOOH , H_2CO , CF_4 , OCS ,) recorded at KPNO on earlier dates. Molecular parameters for a number of molecules were obtained from which several papers were published or are in preparation.

Improved line lists of N_2O , NO_2 , H_2O , CH_4 and CO_2 were created from the analysis of laboratory measurements. In addition, assistance was given to ongoing studies of O_3 , COF_2 , and H_2O_2 that were previously initiated by other investigators. Also, in response to the needs of ATMOS, analyses of some heavier molecules (HNO_3 , COF_2 , CF_4 and several chlorofluorocarbons) were performed in spectral regions of stratospheric interest in which empirical fits of the laboratory data were obtained. The latter is an ongoing task and will continue.

E. PUBLICATIONS

1. J. P. Champion, J. C. Hilico and L. R. Brown, "The vibrational ground state of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$," J. Mol. Spectrosc. 133, 244-255 (1989).
2. J. P. Champion, J. C. Hilico, C. Wenger and L. R. Brown "Analysis of the ν_2/ν_4 Dyad of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$," J. Mol. Spectrosc. 133, 256-272 (1989).
3. L. R. Brown, M. Loete and J. C. Hilico, "Line strengths of the ν_2 and ν_4 bands of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$," J. Mol. Spectrosc. 133, 273-311 (1989).
4. R. A. Toth, E. A. Cohen and R. L. Poynter, "Line frequencies and absolute strengths in the (010)-(000) band of H_2^{16}O ," J. Am. Opt. Soc. (in press).
5. L. R. Brown and E. A. Cohen, "Assignment of the ν_1 and $2\nu_2$ bands of COF_2 at $5.2\ \mu\text{m}$," 44th Symposium on Molecular Spectroscopy, Abstract RE7, Ohio State University (1989).
6. R. A. Toth, "New measurements and analysis of H_2^{16}O , H_2^{17}O and H_2^{18}O in the $6.2\ \mu\text{m}$ region," 44th Symposium on Molecular Spectroscopy, Abstract TE12, Ohio State University (1989).
7. R. A. Toth, "Line strengths ($1100\text{-}2370\ \text{cm}^{-1}$), self broadened line widths and frequency shifts ($1800\text{-}2630\ \text{cm}^{-1}$) of N_2O (submitted to J. Am. Opt. Soc.).

A. LASER LABORATORY SPECTROSCOPY IN SUPPORT OF ATMOSPHERIC MEASUREMENTS

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C. Abstract of Research Objectives

The laser laboratory spectroscopy program involves the acquisition and analysis of high-resolution molecular spectral data which are required for the interpretation of atmospheric measurements by infrared instruments such as the BLISS and ALIAS diode laser spectrometers and FTIR instruments. These data are also required to define the optimum spectral regions to be used for detection of a particular molecular species, to establish the feasibility of new spectroscopic techniques for in-situ and remote sensing of Earth and planetary atmospheres, and to test current theories of molecular lineshape variations with pressure, temperature and gas composition.

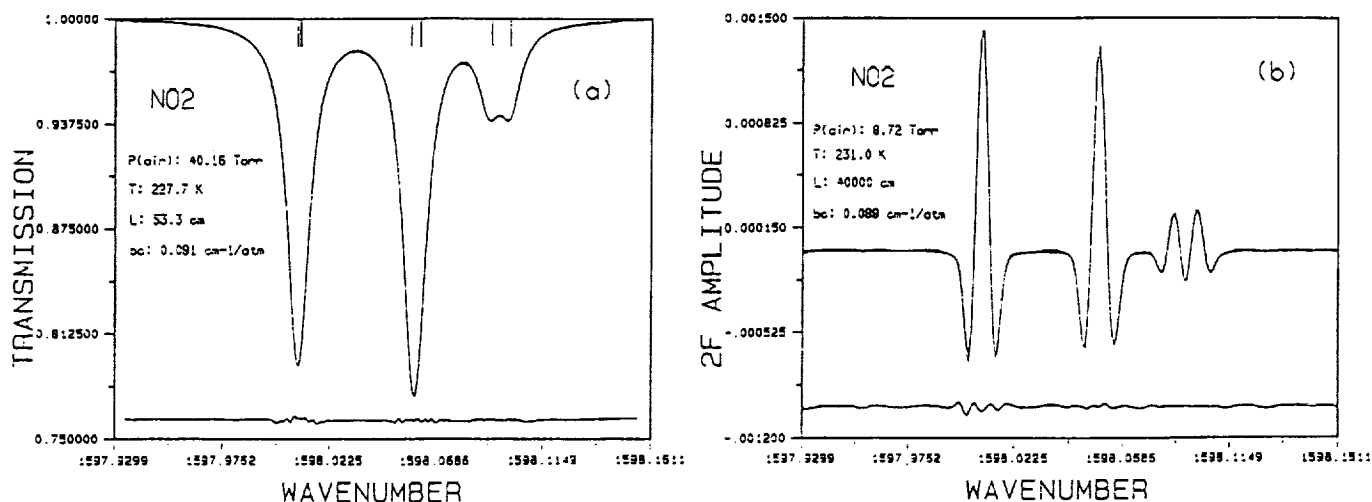
D. Summary of Progress and Results

Measurements have been made, for the first time, of the spectral response of a pressure modulated radiometer using a high-resolution tunable diode laser spectrometer. Recorded lineshapes of selected lines of N_2O , H_2O and $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ were interpreted using one- and two-pressure approximations for the mean and modulated transmission signals, respectively.

A coolable (to 200 K) 1/2 m absorption cell was constructed and used to measure collisional line broadening coefficients for several molecular species important in stratospheric photochemistry. Air-broadening coefficients were measured as a function of temperature for NO_2 near 1600 cm^{-1} , HNO_3 in the $1290 - 1340\text{ cm}^{-1}$ region, and O_3 near 1065 cm^{-1} . For HNO_3 , line positions and intensities were also measured for approximately 1000 lines in the 7.5 micron bands to provide data needed for completion of the rotational analysis of the overlapping ν_3 and ν_4 bands. These measurements were utilized in the analysis of data from two recent flights of the BLISS balloon-borne diode laser spectrometer.

A complete set of data acquisition and analysis software has been developed for recording and processing infrared spectral data on a laboratory minicomputer. Sophisticated interactive spectral fitting routines allow

accurate processing of both direct transmission and harmonic diode laser spectra. Currently, implementation of RF modulation techniques, which enable quantum noise-limited detection sensitivities to be realized, is underway with applications in both laboratory and field measurement programs utilizing tunable diode lasers.



Air-broadened transmission (a) and second harmonic (b) NO₂ spectra

E. Journal Publications

1. R.D. May, D.J. McCleese, D.M. Rider, J.T. Schofield, and C.R. Webster, "Tunable Diode Laser Spectral Diagnostic Studies of a Pressure Modulated Radiometer", *Appl. Optics* **27**, 3591 (1988).
2. R.D. May, "Computer Processing of Tunable Diode Laser Spectra", *J. Appl. Spectrosc.*, **43**, 834 (1989).
3. R.D. May and C.R. Webster, "Measurements of Line Positions, Intensities, and Collisional Air-Broadening Coefficients in the HNO₃ 7.5 micron Band using a Computer-Controlled Diode Laser Spectrometer", *J. Molec. Spectrosc.* (submitted, 1989).
4. R.D. May and C.R. Webster, "Temperature Dependence of NO₂ Air-Broadening Coefficients near 1600 cm⁻¹", (in preparation).

A. Title of Research Task

Millimeter and Submillimeter Spectroscopy in Support of Upper Atmospheric Research

B. Investigators

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C. Abstract of Research Objectives

A program of millimeter and submillimeter spectroscopy research is conducted in support of upper atmospheric research. This includes laboratory studies, critical analysis of data from all available sources, generation of line list catalogs, and distribution of results to the field measurement community. The program involves the acquisition and analysis of molecular spectral parameters which are required for the interpretation of data from stratospheric measurements. The laboratory spectral measurements specifically supports the JPL millimeter radiometer instruments. In order to take full advantage of spectroscopic techniques for quantitative atmospheric measurements, emphasis is placed on performing accurate line frequency, line width, and transition moment measurements. A large portion of the spectral data is also of value to other groups which use spectroscopic techniques for atmospheric measurements. This will be cataloged in a continuously upgraded millimeter data base and made available to interested users. Recently this program has provided valuable molecular structural information which has direct bearing on proposed mechanisms for polar ozone destruction. Work in this area will continue.

D. Summary of Progress and Results

Contributions to the JPL "Microwave, Millimeter, and Submillimeter Spectral Line Catalog" continued with entries being added for $\text{CH}_3^{35}\text{Cl}$, $\text{CH}_3^{37}\text{Cl}$, COF_2 , $^{16}\text{O}^{17}\text{O}$ and H_2^{17}O . Significant improvements in the predicted rotational line strengths of O_3 and H_2O have been achieved by careful consideration of vibration rotation interactions. The rotational wave functions for H_2O which were generated during the updating of the catalog have been used to refine the intensity calculations of the ν_2 band in the $1000\text{--}2600\text{ cm}^{-1}$ region. COF_2 ground state parameters have been improved and used in the analysis of the ν_1 and $2\nu_2$ infrared bands.

A new analysis of the microwave, far infrared, and infrared spectra of transitions involving the (010) and (020) levels of O_3 markedly improved the agreement with observations of both positions and strengths in the 700 cm^{-1} region.

The analysis of the linewidth measurements of the N₂ and O₂ broadened O₃ line near 206 GHz was refined so as to be useful for MLS pointing determinations.

The N₂O₅ millimeter wave spectrum is being re-investigated. Some weak lines have been observed and measured for the first time, but the spectrum remains unassigned.

A gas flow reactor for the synthesis of ClO dimer has been used with the submillimeter wave spectrometer. The dimer's rotational spectrum has been unambiguously observed in the millimeter and submillimeter regions. The rotational transitions of the ground and first excited torsional states of the peroxide structure have been assigned for the 35-16-16-35 and 35-16-16-37 isotopic species. All structural parameters have been determined. It has been demonstrated that ClOOCl is the principal product of the ClO gas phase self reaction at low temperature.

E. Journal Publications

1. H. M. Pickett, E. A. Cohen, L. R. Brown, C. P. Rinsland, M. A. H. Smith, V. Malathy Devi, A. Goldman, A. Barbe, B. Carli, and M. Carlotti, "The Vibrational and Rotational Spectra of Ozone for the (0,1,0) and (0,2,0) States," *J. Mol. Spectrosc.*, **128**, 151 (1988)
2. M. Birk, R. R. Friedl, E. A. Cohen, H. M. Pickett, and S. P. Sander, "The Rotational Spectrum and Structure of Chlorine Peroxide," *J. Chem. Phys.*, in press.
3. Y. Koga, H. Takeo, S. Kondo, M. Sugie, C. Matsumura, G. A. McRae and E. A. Cohen, "The Rotational Spectra, Molecular Structure, Dipole Moment and Hyperfine Constants of HOBr and DOBr," *J. Mol. Spectrosc.*, in press.
4. G. A. McRae and E. A. Cohen, "The ν_2 Band of HOBr," *J. Mol. Spectrosc.*, in press.